

Ya	<i>v</i>	<i>etot</i>	<i>mir</i>	<i>prishol</i>	<i>chtob</i>	<i>videty</i>	<i>sontse</i>
I	into	this	world	came	in order	to see	the sun
	<i>I</i>	<i>sinjy</i>	<i>krugozor,</i>				
	And	the blue	horizon,				
Ya	<i>v</i>	<i>etot</i>	<i>mir</i>	<i>prishol</i>	<i>chtob</i>	<i>videty</i>	<i>sontse</i>
I	into	this	world	came	in order	to see	the sun
	<i>I</i>	<i>vjsi</i>	<i>gor.</i>				
	And	the heights	of mountains.				
Ya	<i>v</i>	<i>etot</i>	<i>mir</i>	<i>prishol</i>	<i>chtob</i>	<i>videty</i>	<i>more</i>
I	into	this	world	came	in order	to see	the sea
	<i>I</i>	<i>slavnjy</i>	<i>tsvet</i>	<i>dolin—</i>			
	And	the glorious	color	of the valleys—			
Ya	<i>zaklyuchil</i>	<i>mirj</i>	<i>v</i>	<i>yedinom</i>	<i>vzore.</i>		
I	embraced	the universes	in	one	glance.		
	<i>Ya</i>	<i>vlastelin.</i>					
	I	the master.					
Ya	<i>pobedil</i>	<i>golodnoye</i>	<i>zabveniye</i>				
I	conquered	cold	oblivion				
	<i>Sozdav</i>	<i>mechtu</i>	<i>moyu,</i>				
	Having created	fancy	my,				
<i>I</i>	<i>kazhdjy</i>	<i>mnig</i>	<i>bjl</i>	<i>polen</i>	<i>otkrjteniya.</i>		
And	every	moment	was	full	of revelation.		
	<i>Vsegda</i>	<i>poyu.</i>					
	Continually	I sing.					

GEOCHEMISTRY.—*The formation of colloid from halloysite in dilute acid solutions.*¹ P. G. NUTTING, U. S. Geological Survey.

Intensive soil research of the past few decades has clearly shown the presence in most soils of complex mineral aggregates of siliceous colloids. These aggregates may be either massive, in a filterable clear solution, or coatings on microscopic grains; they may be sol, hydrosol, gel, or solid. They form definite associations with the ions of a solution as reported by Sante Mattson and others in numerous papers in Soil Science. The writer^{2,3,4,5} has reported a number of studies of relations between dilute acids and

clays of the montmorillonite type. Abundant evidence was found for the formation of considerable quantities of stable colloidal hydrosols as well as of salts in dilute acid solutions. To obtain exact quantitative relations between the amount of sol formed and the amounts of acid, clay, and water present, work was continued with the simpler clay minerals kaolinite, halloysite, and allophane under carefully controlled conditions. The allophane available (from Hillsboro, Ohio) reached equilibrium in a few hours but contained 3.5 percent CaO and some iron. The kaolinite, from Bishop, Calif., was very pure but required five days at 96° C. to approach equilibrium.

The halloysite used, from Anamosa, Iowa, contained no detectable Ca, Fe, or Mg. It was room dried and ground to pass a 150-mesh sieve (0.1 mm). As used it contained SiO₂ 42.45, Al₂O₃ 36.02, H₂O 21.53, or

¹ Received January 11, 1944.

² *The action of some aqueous solutions on clays of the montmorillonite group.* U. S. Geol. Surv. Prof. Paper 197-F, 1943.

³ *Time and temperature effects in the formation of colloidal dispersions.* Journ. Washington Acad. Sci. 31: 41-45. Feb. 15, 1941.

⁴ *A study of the association of magnesia with silica in a pure magnesium clay.* Journ. Washington Acad. Sci. 30: 233-237. June 15, 1940.

⁵ *A study of bleach clay solubility.* Journ. Franklin Inst. 224: 339-362. Sept. 1937.

$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3.4\text{H}_2\text{O}$. The alumina was completely soluble in a few hours in 20 percent acid. Special tests showed that 72 hours at 96° in 0.1 percent acid gave a close approach to equilibrium, while at 30° six months would have been required⁶ for each run. The relations between the amount of sol and the amounts of clay, acid, and water are, of course, very different at the two temperatures, but apparently only the constants of the reaction equation are affected.

Preliminary runs showed that the center of interest is sufficient acid to dissolve the alumina (0.75 gram HCl per gram of halloysite) in sufficient water to dissolve the silica (1 liter per gram of clay), or a gram of clay in a liter of 0.075 percent HCl. Preparations were made with $\frac{1}{2}$, 1, and 2 times these amounts of clay, acid, and water, 27 in all (or 19 excluding simple multiples) which were analyzed.

After 72 hours at $96^\circ \pm 1^\circ$, the last 16 hours without stirring, the clear liquor was decanted with an aspirator flask and the undissolved clay filtered, washed, ignited and weighed. A few ml of the decanted liquor was cooled for pH determinations. Each solution was evaporated and the residue, heated to 160° for an hour to remove free acid and moisture without disturbing OH, and then weighed. Each residue was then boiled 10 minutes in 150 ml of distilled water to remove possible chlorides, again dried at 160° and weighed. Silica and alumina were then separated by a ten minute digestion in about 20 ml of hot 20 percent HCl. Repeated runs gave results duplicating within 2 percent.

Undissolved clay residues varied between 22.9 percent for clay:acid:water = $\frac{1}{2}:1:\frac{1}{2}$ to 91.7 percent for $2:\frac{1}{2}:2$. In composition, they differed but little from the original halloysite. The pH of the solutions varied chiefly with the clay:acid ratio, 2.5 for original clay:acid = 2:1 to pH 1.5 for clay:acid = 1:2. It varies little with the water present, by about 0.02 for half or double the amount of water; hence both the dissociation and hydrolysis of reaction products are but little affected by the amount of water present in this range.

Residues from evaporation of solutions

varied from 0.125 to 0.709 gram per gram of clay, the chief factor being the ratio of acid to clay. In each of the nine sets of observations in which the clay:acid ratio was constant, the amount of residue decreased by one-third as the water alone varied from $\frac{1}{2}$ to 2 liters.

The hot-water extract of the solution residue (150 ml) always caused a loss in weight averaging 20 percent, both weighings following thorough drying at 160° . This extract was neutral to litmus and added ammonia gave no precipitate except in two cases of high acid:clay ratio, hence was free from acid and aluminum chloride. Analysis showed it to be an alumino-silicate hydrosol with an alumina:silica ratio of about 1:1.5 (molar). The solution residue not dissolved by 150 ml of hot water varied from 0.056 to 0.734 gram per gram of original clay as acid varied from $\frac{1}{4}$ to 4 normal ("normal" is 0.75 gram HCl). With clay:acid 1:1, it decreased from 0.375 with water $\frac{1}{4}$ to 0.151 gram for water = 4 liters per gram. An average of the 19 analyses (27 combinations) gave $\text{SiO}_2:\text{Al}_2\text{O}_3 = 0.88$, close to that for $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ (0.884). This ratio varies slightly with the ratio of acid to clay; extremes were 1.1 for acid:clay = 4 and 0.7 for acid:clay = 1:4. The average composition of the washed residue at 160° is SiO_2 34.8, Al_2O_3 40.0, H_2O 25.2 percent or very close to $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 7\text{H}_2\text{O}$, an allophane. Similar runs but less extensive and less exact, made with kaolinite, mica, and allophane instead of halloysite, gave the same allophane hydrosol.

The amount of sol (S) produced, time 72 hours and temperature 96° being constant, depends upon the three independent variables clay (C), acid (A), and water (W). Mere inspection of the 19 analyses yields only the qualitative summary given above. To obtain exact reaction equations between sol, clay, acid, and water, the 27 analyses were plotted in various sets of graphs. In each set, one factor (say clay = 1 gram) is constant throughout, another (say water) is the parameter, constant in each group while the third is the chief variable, the object being to discover linear relationships, if any, between these variables. Three such relations were found:

⁶ *Op. cit.*, footnote 3;

Sol: Acid, clay, and water constant, acid variable.

Log (S:A) linear in log C, water constant.

Log (S:A) linear in log W, clay constant.

These three relations may be combined in

$$\text{Log } S = \text{log } A + a \text{ log } C + b \text{ log } W + \text{const.}$$

With this as a guide the 27 analyses were written as 27 equations which were solved by least square methods to obtain values of the constants. Using natural logarithms the final relation is

$$\text{Log } S = \text{log } A + 0.322 \text{ log } C - 0.318 \text{ log } W - 1.421$$

for grams of sol formed where pure halloysite is brought to equilibrium with dilute hydrochloric acid solutions at 96°. This relation holds for acid:clay ratios below 1:4 (by weight) up to about 4:1 above which free chlorides are formed. All constants depend upon temperature. The clay is in grams, the water in liters, and the acid in multiples of 0.75 gram. For $C=1=W$, $S=0.24 A$, or $75 S=A$ in molar proportions, if the molecular weight of the sol is 510, indicating that the acid is used many times over. Water and clay are evidently in competition for the acid.

The chemical processes involved appear to be very simple. After the clay has adsorbed sufficient anions it is attacked by them. Free silica and chlorides go into solution and the chlorides are hydrolyzed, alumina combining with the silica to form a sol while the free acid returns to the clay to form more chloride. This process continues until the potential of the accumulated sol is balanced by that of the clay. This balance is at somewhat less than half the clay because the halloysite has some

structural energy while the sol has little or none.

SUMMARY

Halloysite in warm dilute acid forms a sol having the composition of allophane $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 7\text{H}_2\text{O}$ after drying at 160° C., over an intermediate range of clay and acid concentrations.

A quantitative relation between sol formed and the acid, clay, and water used is obtained from experimental data covering the range from just sufficient acid to dissolve the alumina and water to dissolve the silica, to half and double these amounts.

At equilibrium, the clay solution contains free acid (pH 1.5 to 2.5) but no salt other than the sol in this range.

With clay and water as parameters, the amount of sol formed is in a fixed ratio to the acid present.

With acid and water as parameters, the sol varies with about the cube root of the clay present, indicating a reversible reaction.

The amount of sol varies inversely with the water present, clay and water competing for the acid present.

After oven drying at 160°, the sol (then gel) is soluble in hot water to the extent of about 0.3 gram per liter, slightly less than than silica gel, 0.4 gram per liter.

A general characteristic relation is deduced between amount of colloid formed and the amount of acid, clay, and water present. In reference 3, p. 45, it was shown that silica, alumina, acid, fluorides, and other salts added to the sol solution were without effect on the colloid formed. Variations with temperature and the nature of the acid remain to be investigated.

ECOLOGY.—*An analysis of the flora of the Bull Run Mountain region of Virginia using Raunkiaer's "life-form" method.*¹ H. A. ALLARD, Bureau of Plant Industry, Soils, and Agricultural Engineering.

INTRODUCTION

Ecologists have long been aware of the intimate relations between plant life and climate and, rightly regarding vegetation as an expression of the climatic complex, have

attempted to devise methods to express this concretely and statistically in terms of plant life itself. Long ago Humboldt (*Physiognomik der Gewächse*, 1806) attempted to classify vegetation on something of an ecological basis. Griesbach (1872) and others building upon these concepts recognized

¹ Received November 6, 1943.